Wintertime Reactive Nitrogen Chemistry During the 2015 WINTER Aircraft Campaign

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MOTIVATION: Influence of Nocturnal Chemistry on Wintertime NO3 and O3 Budgets

Why Nocturnal Chemistry?
- Aerosol (< 1um) chloride, nitrate, ammonium, sulfate, organic content (AMS–NO3)
- N2O5 and ClNO2 production from the oxidation of NO3 (< NO2+ NO3) in the presence of volatile organic compounds (VOCs) reaction with residual NO3 at night leads to NO3 titration
- NO3, heterogeneous chemistry can lead to net NO3 and NO3 loss or downward transport and halogen activation depending on its uptake efficiency to aerosol and partitioning between products

N2O5 Heterogeneous Chemistry

N2O5 + Aerosol Reservoir → ClNO2 + NO3 +... Produced in gas phase from ClNO3 splitting

Tropospheric Influence and Remaining Uncertainties of NO3 Heterogeneous Chemistry

Limited observations of γh and a:
- Historically, γh = 1.0 and a = 0 (i.e. Tie et al., JGR 2003) – NO3 heterogeneous chemistry contributes to ~50% and ~10% reductions in total wintertime column NO3 and O3, respectively
- Servar et al., GRL 2014 included ClNO3 production to aerosol O3 over U.S. increased by ~10%
- Meint and Evans, ACP 2010 - O3, O3, and NO3 budgets most sensitive (up to 40%) to changes in γh in observed range of 10−1

Remaining Uncertainties:
- Further constrain the variability in observed γh and a
- Determine how the diffusion factors (i.e. pH, aerosol composition, RH) influence the observed γh and a

Adapted from Figure 3 in Servar et al., 2014. Change in tropospheric γh with the inclusion of ClNO3 production and Cl chemistry in CMAQ global model

ANALYSIS METHOD: Simple Chemical Box Model

Method: Simulate the chemical evolution of an air parcel from sunset until the time of aircraft measurement, while fitting to NO3, O3, NO2, and ClNO3 observations to derive γh and a

Step 1: Derive Initial NO3 and O3
- Adjust initial [NO3] and [O3] until final simulated values are within 1% of measurements

Step 2: Derive Total NO3 Loss Rate (kNO3)
- Adjust total NO3 loss rate until final [NO3] is within 1% of observed value in Appendix A

Step 3: Use total loss rate to derive production rate of ClNO3 (kClNO3)
- Hold kNO3 constant and iteratively change ClNO3 until final [ClNO3] is within 1% of observations

Step 4: Use derived kNO3 and ClNO3 to calculate γh, a, and nocturnal soluble nitrogen

Box Model Sensitivities and Uncertainty

1. Simulation Start Time – Chemical Clock based on observed NO2/NO3 ratios:
   - Total kNO3 = kNO3 uptake + kNO3 deposition + kNO3 formation

2. Diurnal/Ocean Deposition – Box model-derived Total kNO3 loss is equal to:
   - Total kNO3 = kNO3 uptake + kNO3 deposition + kNO3 formation

3. NO3 Measurements –
   - NO3 instruments agree to within ±14%

WINTER Campaign and Modeling

WINTER: Wintertime Investigation of Transport Emissions and Reactivity
- 13 Research flights during February and March 2015 on the eastern U.S.
- Research flights sampled marine, coastal, and interior environments
- Mix of day, day-into-night, night, and night-into-day flights

6-Channel Cavity Ring-down Instrument
- N2O5 via thermal dissociation to NO2 and subsequent subtraction of NO2 channel
- NO2 via thermal dissociation into NO2 and NO3, and subtraction of NO3 channel
- NO3, O3 additions of NO or O3 to convert to NO3 and subsequent subtraction of NO3 channel

Measurements Used to Inform Box Model
- Reactive nitrogen oxides (CRDS – NOAA, TD-LIF – UC Berkeley, Chemiluminescence – NCAR), Ozone (CRDS–NOAA), Nitrile Chloride (HERFPIMS – U. Washington), Speciated VOCs (TOGA–NCAR), Aerosol Surface Area (Derived from UCams/PCASP – NCAR), Photoysis rates (Filter Radiometer – NCAR)

Additional Data for Analysis of Box Model Results
- Aerosol (< 1um) chloride, nitrate, ammonium, sulfate, organic content (AMS–U. Colorado), aerosol (<10um) chloride and nitrate (U. New Hampshire), aerosol pH (Georgia Tech), Meteorological Data (NCAR C-130, HNO3, (HERFPIMS – U. Washington)

Preliminary Results: Trends in Modeled NO3 Heterogeneous Chemistry

Research Flight 04 – Feb 11 2015
- Central East Coast
- Median γh = 0.023, Median a = 0.1
- Min, Max, Avg NO3 (ppbv) = 0, 12, 0.04
- Min, Max, Avg ClNO3 (ppbv) = 0, 1.2, 0.01

Research Flight 08 – March 01 2015
- Offshore New York
- Median γh = 0.004, Median a = 0.1
- Min, Max, Avg NO3 (ppbv) = 0, 2.2, 0.41
- Min, Max, Avg ClNO3 (ppbv) = 0, 2.3, 0.46

SUMMARY, FUTURE WORK, AND ACKNOWLEDGMENTS

1. Field measurements from the WINTER aircraft campaign have been used to inform and constrain a chemical box model that has been used derive two governing parameters of NO3 heterogeneous chemistry that impact regional tropospheric oxidant budgets.
2. The box model is most sensitive to the simulation start time, uncertainties in additional NO3 loss processes, and measurements of NO3.
3. Preliminary model results show an order of magnitude difference in median γh values from two different research flights; expected trends in γh and a with aerosol composition and pH are potentially suppressed when γh is small.
4. Future work includes minimizing model uncertainties, completing simulations for all research flights, and determining γh and a relationships to environmental conditions.

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